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MEMORANDUM

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PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

DATE:

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SUBJECT:

Exposure of Individuals to Chlorpyrifos following Turf Treatment with a

Granular Product (MRID No. 44167101)

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Title:	Chlorpyrifos: Exposure to Adults and Children Upon Re-Entry to Domestic Lawns Following Treatment with a Chlorpyrifos-Based Granular Insecticide
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MRID Number:	44167101 (DP Barcode: <u>D233282</u>)
Sponsor Facility:	Dow AgroSciences (formerly DowElanco)
Performing Facility:	Midland Industrial Hygiene Service Center, Health and Safety Services, The Dow Chemical Company, Midland Michigan
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1.0 INTRODUCTION

DowElanco has submitted a study measuring environmental levels of chlorpyrifos and exposures of individuals performing activities on residential or recreational turf following treatment of the turf with a granular product. The study was patterned after a study conducted with a liquid formulation that has previously been reviewed by the Agency (Jaquith 1996).

2.0 EXECUTIVE SUMMARY

Nine volunteers performed activities intended to mimic a child walking/running, sleeping, crawling and sitting on turf following application of a granular formulation of 0.5% chlorpyrifos at a rate of 1.8 lb active ingredient (ai) per acre. The volunteers performed the activities for a period of four hours, beginning immediately after the insecticide application. Touch football (1 hour) and frisbee (1 hour) were used to mimic a child walking/running, while weeding activity (30 minutes) was used to evaluate a child crawling on the lawn. The other two activities included picnicking on a towel for 1 hour, and sunbathing on a towel for 30 minutes, which estimated exposure from sitting and lying down. During each activity, each participant wore only a T-shirt and shorts. Running shoes were added during touch football to prevent injury.

Absorption of chlorpyrifos was determined by monitoring the amount of metabolite 3,5,6-trichloro-2-pyridinol (3,5,6-TCP) excreted in the urine over an average of 5.5 days following exposure. Based on the biomonitoring and environmental data collected in this study, the mean exposure to 8 adults (4 male and 4 female), corrected for background exposure is $1.4 \mu g/kg$ with a range of 0.56 to 3.7 $\mu g/kg$. The results from one adult (volunteer J) were excluded from the mean calculation because estimated background exposure exceeded overall exposure from the activities on the treated lawn. The method used to estimate exposures directly measures internal dose and does not differentiate between routes of exposure.

The adult chlorpyrifos exposure estimates were then extrapolated to estimate potential exposures to children. For this extrapolation, the registrant subtracted the estimated respiratory exposure contribution from the total exposure, yielding an estimate of dermal exposure. The estimates of exposure via the dermal route were then adjusted to account for surface area differences between adults and children. Oral exposure via hand to mouth activity was estimated by assuming that all of the pesticide removed by hand rinse was available for ingestion. For child exposures, the adult oral exposure estimates were also adjusted to account for the hand surface area differences between adults and children. EPA also used this approach to estimate child exposures. The extrapolated estimate of child exposure (1-6 yrs old) based on the adult data is a mean of $2 \mu g/kg$, with a range of 0.75 to $5.1 \mu g/kg$. This extrapolation to a child may underestimate exposure because it neglects incidental ingestion of granules and/or soil. In addition, based on the deposition measurements, only 75% of the theoretical recommended label rate was applied to the field where exposure activity occurred. Consequently, the exposures estimated in this study may underestimate exposures to residents that apply granular insecticides containing chlorpyrifos at the recommended label rate. However, the application rate used in this study is considered

appropriate, and within the application varibility that is expected for the equipment used in this study.

There are a number of uncertainties associated with exposure monitoring in the residential environment: 1) It is not known how well the activities conducted during this study relate to the activity patterns of the general population; 2) hand/oral exposure may in fact be somewhat different from estimates by using the assumption that all of the residue measured by the hand wash technique is available for oral exposure. The actual contribution from the oral route is unknown and may be more or less than estimated. The factors used to extrapolate the indirect measurements to account for child exposure contains some error. Combination of these errors from various factors and assumptions contributes to the total error in the exposure assessment. It is EPA's view that the biomonitoring data, with the addition of the hand rinse residues, provides the best estimate of the exposures of children. Additional uncertainties associated with these estimates include possible differences in dermal absorption and age-related differences in metabolism of chlorpyrifos and in activity patterns. In lieu of extensive data addressing the above uncertainties, EPA considers this study to provide a reasonable estimate of the potential exposure of individuals, both adults and children, to chlorpyrifos following application of granular chlorpyrfios insecticide to turf:

Environmental measurements were also collected during the study. Dislodgeable residues, as measured by the drag sled, decreased with time. Mean dislodgeable residues were 5.6 and 4.56 $^{-}$ $\mu g/ft^2$ for the high and low pressure drag sleds, respectively one hour after application and fell to means of 0.42 and 0.44 $\mu g/ft^2$, respectively by day 4 post application. This supports the idea that dislodgeable residues fall rapidly after treatment.

As expected, air concentrations peaked within 2-4 hours after application and continued to decline in the remainder of the 4 days post application. The peak concentrations were 1.06 and $12.4 \,\mu\text{g/m}^3$ for 15 and 60 inch heights, respectively. The concentrations measured at 4 days post application were 0.52 and not detected (ND, <0.28) $\mu\text{g/m}^3$ at heights of 15 and 60 inches, respectively.

3.0 DETAILED CONSIDERATIONS

3.1 Test Material and Site Description

A granular formulation of chlorpyrifos containing approximately 0.5 percent active ingredient was applied to a 200 ft x 200 ft area of turf using a Lesco rotary spreader. The grass was approximately 3 inches in height. The test material was made by adding a 66 percent solution of chlorpyrifos in xylene to ground corncobs and allowing the solvent to evaporate. This was applied to the turf at a rate of 1.8 pounds of active ingredient per acre (327.8 lbs of formulation per 0.92 acres). The turf plot was divided in half, forming two 100 ft x 200 ft subplots. One half was used for physicochemical evaluation and the second for the activity pattern portion of the study.

3.2 Physicochemical Measurements

3.2.1 Deposition

Forty small aluminum plates were randomly placed on both halves of the plot prior to application to evaluate the uniformity of the treatment. Following application the contents of the plate were rinsed into a vial with ethyl acetate: The vials were stored on ice for transport to the analytical laboratory and kept in a freezer prior to analysis.

3.2.2 Dislodgeable Residues

Ten mini-areas were designated for dislodgeable foliar residue analysis in the physicochemical (PC) subplot. Each mini-area contained a plywood template with six 48-inch by 4-inch cutouts to guide a drag sled with a weighted denim coupon ("Dow sled" described previously in Jaquith 1996). This system has been used to determine dislodgeable residues on carpet surfaces as well as on turf (Jaquith 1995). The system uses a lead weight on a 3" x 3"x 3/4" plywood block. Two weights were used; low pressure to imitate the pressure from a 10 kg child (0.9 lb/in²), and a second higher pressure intended to imitate a standing adult female weighing approximately 120 lb (1.5 lb/in²). Six drag samples, 3 high and 3 low, were collected from randomly selected mini-areas 1 hour after application and at intervals of 2, 4, 8, 24, 48, 72, and 96 hours after the treatment. Only one drag was conducted in any given lane. Each drag sample consisted of a single pass over the treated area. Moistened denim coupons were attached to the drag sled to imitate human skin. Each drag coupon was stored in vial on ice and transported to the lab, where the samples were stored in a freezer prior to analysis.

3.2.3 Air Sampling

Air samples were collected in the center of the treated area at heights of 15 inches and 60 inches, reflecting the breathing zones of a lying and standing adult, respectively. Air concentrations of chlorpyrifos were determined by drawing air through sampling cassettes at a rate of one liter per

minute using battery operated pumps. The sampling cassettes consisted of cellulose membrane filters (GN-4) to capture dust, backed up by tubes containing Chromosorb 102 to trap any vapors. The sampling period was approximately one hour except during the activity period (described below) when a 2.7-hour time weighted average (TWA) was determined at both heights. Sampling took place immediately after application (T0) and at intervals of 1, 2, 4, 8, 24, 48, 72, and 96 hours. Sampling tubes and cassettes were also stored on ice for shipment to the analytical laboratory and stored frozen until analysis.

3.2.4 Foliar Residues

In order to estimate the dissipation of chlorpyrifos from turf foliar residue samples were collected 1 hour after application and at intervals of 2, 8, 24, 48, 72, and 96 hours post-treatment. Three replicate samples were collected at each interval. A 2.75 in² area was snipped with scissors and placed in a tared glass jar. The samples were kept closed until returned to the laboratory. In the laboratory the jars were opened and placed in a humidity chamber, maintained at 50% relative humidity for one hour to allow evaporation of surface moisture. The jar was then capped and weighed to determine the weight of grass. After this process the sample was kept frozen until analysis.

The samples were shaken with two 40 ml aliquots of anionic surfactant solution (0.008% dioctyl sodium sulfosuccinate, DSS) to remove the granular formulation from the surface. After the soap mixture was decanted into a jar, 4.8 g of sodium chloride was added, followed by shaking with two 30 ml aliquots of ethyl acetate. The ethyl acetate phase was analyzed for chlorpyrifos.

In order to obtain useful dissipation data, determination of the surface area of the samples was necessary. The relationship of the grass weight to surface area was determined by the use of a regression curve. Grass samples of known weight were placed in a Leaf Area Meter (Ll-3100) with an accuracy of 0.001 cm². The surface area of samples and the relationship of surface area to weight of grass was determined prior to the field portion of the study. One extra sample was included with each set of samples to check the surface area vs. weight.

3.3 Analytical Methods

The analytical methods used for this study were previously validated and used for earlier studies (Jaquith 1995, 1996, Firestone 1988). Method validation data were not provided in this report although blanks and knowns were included. The 37 mm (GN-4) filters were connected in series with Chromosorb 102 tubes (66 mg front section, 33 mg back section). The filters and tubes were desorbed separately by mechanically shaking with 5 ml hexane at low speed for 1 hour. Extracts were analyzed by capillary gas chromatography with an electron capture detector (GC/ECD). The reported recoveries for this method were $94.1 \pm 7.11\%$ and $100.8 \pm 9.21\%$ for the filters and tubes, respectively. The denim patches used for dislodgeable foliar monitoring were extracted with 30 ml of iso-octane in the same manner as the air sampling media and analyzed by GC/ECD. The reported recoveries for this method were $102 \pm 6\%$.

Hand and leaf wash samples were also evaluated using a previously validated method. A surfactant solution was used to wash the surfaces followed by extraction with ethyl acetate. The ethyl acetate extract was analyzed by GC/ECD. The reported recoveries were $104 \pm 9.0\%$. The registrant experienced some difficulties in use of the hand/leaf wash method when assessing the granular formulation. When the granular formulation was combined with the wash solution as described above, only $\sim 30\%$ of the chlorpyrifos was extracted compared to approximately 100% when ethyl acetate was used alone. The registrant theorized that water was being absorbed by the corncob granules and providing a barrier between the chlorpyrifos and the ethyl acetate. The registrant does not believe that large granules would adhere either to the skin or the leaf surfaces but rather that the contamination of these surfaces would be the result of dust or dislodged chlorpyrifos. These should be readily extracted from the wash samples.

Sample chromatograms submitted with the report indicated that resolution of chlorpyrifos from the solvent front interferences were acceptable. The dynamic range of the ECDs was about 0.125 to 12.5 μ g/ml with a quantitation limit of ~0.003 μ g/ml based on a signal to noise ratio of 6 and a 1 μ L injection volume.

3.4 Human Activity Monitoring

Human activity monitoring was conducted on the second 20,000 ft² subplot. Five different activities were selected to represent the behavior of individuals on the treated turf and began immediately after application. Activity started with one hour of picnicking activity (sitting on a 'towel). This was followed by three hours of activities, carried out in 15 minute intervals. The order of these activities is presented in Table A. Touch football and frisbee were used to mimic a child walking/running and sunbathing represented a child sleeping. The weeding activity was supposed to imitate a child crawling on the turf, while picnicking on a blanket, represented a child sitting. During the activity period, each participant wore only a T-shirt and shorts. Running shoes were added during the touch football to prevent injury. Each volunteer was instructed to wait at least 4 hours following the activity period before showering to allow absorption of any chlorpyrifos from the skin and increase consistency of the results.

Activity S	Schedule for Volunte Form	Table 1 ers on a Grass Sui ulation of Chlorp		a Granular
		15-Minut	te Interval	
Hour	1	2	3	4
1	Picnicking (on a blanket)	Picnicking (on a blanket)	Picnicking (on a blanket)	Picnicking (on a blanket)
2	Frisbee	Weeding	Frisbee	Weeding
3	Frisbee	Frisbee	Touch Football	Touch Football
4	Sunbathing	Sunbathing	Touch Football	Touch Football

3.5 Hand Rinse

At the end of the activity period the hands of each subject were rinsed with a dilute solution of the surfactant, dioctyl sodium sulfosuccinate (DSS). The persons hands were held over a bowl and doused with 250 ml of the solution in 3 aliquots. This wash was followed by a rinse with 250 ml of deionized water, also in 3 aliquots. The bowl was rinsed with ethyl acetate (200 ml) and combined with the aqueous phase. Sodium chloride (15 g) was added to facilitate phase separation and the liquids were vigorously shaken. Two aliquots of the ethyl acetate phase were stored on ice for shipment to the laboratory where they were stored in a freezer until analysis.

3.6 Biological Sampling

3.6.1 Blood Sampling

Blood samples (approximately 5 ml) were collected from each volunteer on 2 separate days during the week prior to the study. Samples were again collected approximately 24 and 48 hours after the start of study. The blood samples were analyzed for plasma cholinesterase activity by the medical division of Dow Chemical Company.

3.6.2 Urine Collection

All urine voided was collected on the day prior to the start of the study and for up to six days after the study commenced. Each daily sample was collected as two specimens, each representing the total urine voided during a 12 hour period. The first collection period started after the first voiding in the morning and ended at approximately 7 PM. The second collection began with the first voiding after this time and ended with the first voiding the next morning. Urine voided at the start of the first pre-study collection period was discarded. Urine voided at the start of each

succeeding period was added to the previous intervals total. Specimens were collected at ambient temperatures in 4-liter amber Polypac containers.

The specimens were weighed upon receipt and the volume calculated by weight, assuming a specific gravity of 1.0. Aliquots were removed, transferred to glass containers, and stored frozen until analysis for creatinine and 3,5,6-trichloro-2-pyridinol (3,5,6-TCP), a metabolite of chlorpyrifos. To document that 3,5,6-TCP was not lost during storage or analysis, pre-study urine samples were fortified and analyzed with the study specimens.

3.6.3. Analysis of Urine Samples

The samples were allowed to equilibrate to room temperature. Aliquots of these along with separate spiked control urine samples, were hydrolyzed with concentrated hydrochloric acid for 2 hours. The hydrolyzed aliquots were then extracted with 2 ml of toluene and the toluene layer was transferred to a 2 ml autosampler vial. The toluene extract was derivatized by adding 50 μ L of N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA) and heating at 60°C for 1 hour. The samples were then analyzed by gas chromatography/negative-ion chemical ionization/mass spectrometry (NCI-GC/MS) to determine the amount of 3,5,6-TCP.

3.7 Analysis of Urinary Data

The completeness of urine collection was determined by analysis of the creatinine content of the urine samples. The creatinine concentration and urine volumes were used to determine total creatinine output. This was then normalized by the subject's body weight. The resulting values were compared to standard literature values of 14 to 26 mg/kg/day (Tietz 1982). The results were also compared to other samples from the same individual for consistency. Urine collection was considered complete if the creatinine excretion was within or exceeded the normal range and if the excretion rate was consistent within that individual. Individual urine data are presented in Appendix A.

4.0 RESULTS AND CALCULATION OF EXPOSURES

4.1 Biological Monitoring (Direct Methods)

4.1.1 Blood

As noted previously, two blood samples were collected on separate days from each participant during the week prior to the conduct of the study. Additional 5 ml samples were collected approximately 24 and 48 hours after the exposure period. These samples were analyzed for plasma cholinesterase activity using the Kodak analyzer methodology. Collections and assays were performed by the Medical Department of the registrant. Table 2 summarizes the average pre-study and 24- and 48-hour post-study measured plasma cholinesterase levels.

Table 2 Measurements of Plasma Cholinesterase in Volunteers Exposed to Granular Chlorpyrifos Applied to Turf								
Volunteer	Gender	Pre-Study Average Baseline I.U.	24 Hour I.U.	% of Baseline	48 Hour I.U.	% of Basoline		
G	М	8078	72 87	90	7696	95		
Н	М	13185	11668	88	No Sample	No Sample		
I	М	9641	8961	93	9885	103		
J	М	9652	9171	95	9409	97		
K	М	9021	7986	89	7985	89		
L	F	6867	6878	100	6989	102		
М	F	7813	6964	89	6896	88		
N	F	5019	5254	105	5469	109		
0	F	6104	5832	96	5994	98		
Mean		8375	7778	94	7560	- 98		

As shown on this table, the mean cholinesterase baseline for male volunteers (9915 I.U.) was 35 % higher than the mean baseline for females (6451 I.U.). All values were within the normal range of 4,650 to 12,220 I.U. based on the colorimetric methodology, except volunteer H who had an average baseline slightly above normal. Plasma cholinesterase activity was reduced on average 6% and 2% from pre-exposure values at 24 and 48 hours post-exposure, respectively. Males exhibited slightly more inhibition than females (mean reduction of 9% and 4% at 24 and 48 hours post exposure, respectively). At 24 hours post exposure, the overall range of plasma cholinesterase activity was a 12% decrease (volunteer H) to a 5% increase (volunteer N), while at 48 hours, activity ranged from a 12% decrease (volunteer M) to a 9% increase (volunteer N). The registrant failed to explain why a 48 hour post exposure sample was not collected for volunteer H. As shown on Table 3, this volunteer had one of the highest chlorpyrifos exposures of the 9 volunteers, and a 48 hour measurement would have been useful.

4.1.3 Estimation of Exposure from Urinary 3,5,6-trichloro-2-pyridinol (3,5,6-TCP) Measurements

The registrant calculated exposures from urinary metabolites using two separate methods. One method is based on urinary output and the other is a kinetic model. Both methods resulted in

similar estimated exposures, however, the registrant used the higher of the two methods to estimate chlorpyrifos exposure. The first method was derived from a one compartment model designed to describe the time course of 3,5,6-TCP excretion in volunteers after administration of chlorpyrifos to their forearms (Nolan et al. 1984). This model indicates that 70-72 percent of the orally administered chlorpyrifos is excreted in the urine as 3,5,6-TCP, and that the absorption and elimination constants from this study are 0.0308/hr and 0.0258/hr, respectively for dermal exposure. The elimination rate constant is identical for oral exposures (Nolan et al. 1984).

The second method estimated the absorbed dose by dividing the cumulative amount of the metabolite 3,5,6-TCP excreted by the fraction 0.37. This factor represents the ratio of the molecular weights of 3,5,6-TCP (198) and chlorpyrifos (350.6) (i.e., 198/350.6 = 0.56) and the fraction of the absorbed chloripyrifos dose expected to be excreted in 6 days (0.656). EPA used this approach to calculate exposure, but modified the fraction to 0.36 to account for urinary excretion of 3,5,6-TCP 5.5 days (133 hours) post exposure (0.639) using the model equation presented in Appendix B. This time interval represents the average period during which urine was collected following exposure (Appendix A). The pharmacokinetic model used to determine the portion expected to be excreted is presented in Appendix B. The registrant used a computer program to estimate the cumulative percent of excretion at differing time intervals. EPA has previously duplicated these predictions, within rounding error, using a personal computer spreadsheet program (Jaquith 1995). The estimates of total chlorpyrifos absorption based on urinary excretion data are presented in Table 3.

The estimated dose was calculated as follows:

Estimated chlorpyrifos dose (
$$\mu$$
g) = μ g TCP excreted x 350.6 μ g Chlorpyrifos 0.639 198 μ g TCP

= μ g TCP excreted x 2.7 or μ g TCP excreted ÷ 0.36

A correction was also made for the presence of 3,5,6-TCP in pre-study urine samples. Although the participants were instructed to avoid exposure to chlorpyrifos for at least a week prior to the study, measurable quantities of 3,5,6-TCP were found in pre-study urine specimens. These pre-study urine levels were considered to represent background and the participants were assumed to have had some unknown steady state exposure to chlorpyrifos. This steady state exposure would be expected to provide some, relatively constant, contribution to the total 3,5,6-TCP excreted during the six days after study exposure. The excretion data were therefore, corrected to determine the exposure to chlorpyrifos associated with the study exposure. If the background exposure is constant, the amount excreted in the urine per day can be used to estimate the daily exposure by dividing by the proportion excreted in urine (0.72) and the ratio of molecular weights as described above (Jaquith 1996). For example subject G (weighing 79.45 kg) excreted 13.71 μ g of 3,5,6-TCP on the day prior to the study. His background exposure would be:

13.71 μ g 3.5.6-TCP/day x (350.6 μ g chlorpyrifos/198 μ g 3,5,6-TCP) \div 0.72

= 33.7 μ g chlorpyrifos/day or 0.42 μ g/kg/day

The registrant then corrected the total excretion of 3,5,6-TCP to account for this background level. It was assumed that the background excretion remained constant throughout the sampling period of approximately 6 days. The total amount of 3,5,6-TCP excreted was adjusted to account for this phenomenon. The formula for this correction was:

Corrected 3.5.6-TCP Excretion = [Cumulative 3,5,6-TCP excretion - (5.5 days x pre-study excretion)/0.36]

where:

Cumulative excretion = μ g 3,5,6-TCP excreted during the post-exposure sampling interval (133 hours or approximately 5.5 days)

Pre-Study excretion = μg 3,5,6-TCP excreted on the day before the study

The amount of chlorpyrifos absorbed could not be estimated for volunteer J because similar amounts of 3,5,6-TCP were excreted in the pre-study and post-study urine specimens, hence there was not apparent increased exposure from the lawn activities. Therefore, the results from this individual was excluded in the calculation of average chlorpyrifos exposure. The registrant also excluded the results of volunteer O from their analysis because they claim that the excretion of 3,5,6-TCP in urine did not exceed pre-study results until post exposure day 4, and the TCP excretion did not correspond to the pharmacokinetic model. EPA included this volunteer, because 3,5,6-TCP excretion exceeded pre-study excretion on post exposure day 2, and because a number of other volunteers (H, J, and L) had peak excretion of this metabolite on post exposure day 4. It is possible that the delay in excretion can be attributed to the lag time for dermal absorption.

The registrant determined that six of the urine samples were either incomplete or erroneously place in the wrong sampling container based on the creatinine output rate. Correction of these six samples was achieved by multiplying the amount of 3,5,6-TCP in the specimens by the ratio of the mean creatinine excretion rate for that individual to the amount in that particular specimen. Application of this correction factor would have resulted in only minor changes in the total 3,5,6-TCP excretion of 1.38 to 10.9 μ g of 3,5,6-TCP (mean of 4.13 μ g per volunteer), or approximately 0.02 to 0.13 μ g/kg of absorbed chlorpyrifos. Due to the small amount of this dose, no correction for incomplete urine was used, resulting in slight underestimates of chlorpyrifos exposure.

As shown on Table 3, the 8 individuals absorbed on average 1.4 μ g/kg of chlorpyrifos (0.53 to 3.7 μ g/kg). As noted previously, the results from volunteer J were excluded in calculating the average exposure.

4.2 Indirect Measurements

4.2.1 Total Deposition

Deposition was calculated by measuring the contents of forty 5-in aluminum tins (4-in diameter base). As noted previously, the tins were collected immediately after application, rinsed into 40 ml vials with ethyl acetate, and kept frozen prior to analysis. Each tin had a surface area of 0.19 ft². The desired application rate was 2 lbs ai/acre, which is equivalent to 400 lbs of 0.5% chlorpyrifos based granules per acre. However, only 327.8 lbs of 0.5% insecticide were applied to 0.92 acres, resulting in approximately 1.8 lb ai/acre, or 90% of the theoretical labeled rate. Only 4% of the test material were considered "fines" and passed through a 40-mesh screen.

The average deposition was 75% or 15.63 mg of the theoretical amount resulting from the application of 2 lb ai/acre (20.84 mg) and approximately 83% of the applied rate. The average deposition in the physicochem area was 20.51 mg or 98% of the theoretical rate. The raw data were not included in this report. The deposition appears to be within the range to be expected when a chemical is applied to a lawn using conventional lawn care equipment.

4.2.2 Dislodgeable Residues

Dislodgeable residues were determined by dragging a weighted block over one square foot of turf (36 in x 4 in) at three different locations at each of the 8 time intervals. Two different pressures were used, one to imitate the force of a child and the other to mimic the force of an adult female. The results of this drag sampling are presented in Table 4. Initially after application the high pressure sampling dislodged slightly higher residues of chlorpyrifos than the low pressure (at 1 hour 4.56 vs. 5.58 μ g/ft², at 2 hours, 2.45 versus 2.91 μ g/ft², at 4 hours 0.97 vs.

	E	stimated Ab	sorption of	Chlorpyrifos	Following	Table 3 Freatment of	Turf with 1.8	8 lb ai/Acre G	ranular Insec	cticide (a)	•
Subject	BW (kg)	Cumulative 3,5,6-TCP	Pre-Study 3,5,6-TCP 48 Excreted	Pre-Study Chlorpyrifos	Pre-Study 3,5,6-TCP µg/kg/day (b)	Pre-Study Chlorpyrifos Dose µg/kg/day (c)	Cumulative 3,5,6-TCP Excreted (4g) (d)	Chlorpyrifos (48) Uncorrected (e)	Chlorpyrifos (4g) Corrected (f)	Absorption (µg/kg) Uncorrected (g)	Absorption (14g/kg) Corrected (h)
G (M)	79.5	108.7	13.71	24.3	0.24	0.42	95	264	54.6	3.3	0.69
H (M)	73.6	149.9	14.12	25	0.27	0.48	136	378	162	5.1	2.2
I (M)	79.5	123.6	16.70	29.6	0.29	0.51	107	297	42	3.7	0.53
J (M)	81.7	285.7	48.97	86.7	0.83	1.47	237	658	-90	8.1	+1.1
K (M)	74.9	75.6	7.74	13:7	0.14	0.25	68	189	71	2.5	0.95
L (F)	63.6	82.7	9.72	17.2	0.21	0.37	73	203	54.5	3.2	0.87
M (F)	72.6	57.7	6.2 %	11.0	0.12	0.21	52	144	49	2.0	0.67
N (F)	56.8	73.6	6.5	11.5	0.16	0.28	67	186	86.7	3.3	1.53
O (F)	57.2	158.8	12.9	22.8	0.31	0.55	146	406	209	7.1	3.7
Mean	71	124	15.2	26.9	0.3	0.5	109	303	71	4.0	1.4
Std Dev	9.6	70	13.2	23.4	0.2	0.4	58	160	83	2.1	1.1

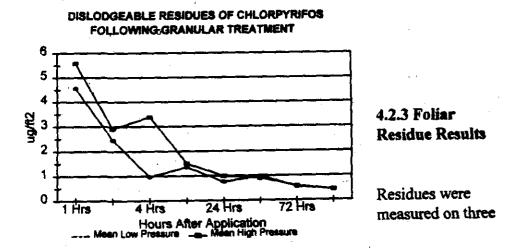
M-Males; F=Females

- (a) Estimates are derived from 3,5,6-TCP excreted in the urine over an approximately six day period after performing activities on the turf.
- (b) Pre-Study 3,5,6-TCP ($\mu g/kg/day$) = Pre-Study 3,5,6-TCP excreted/0.72/BW
- (c) Pre-Study Chlorpyrifos ($\mu g/kg/day$) = Pre-Study 3,5,6-TCP * 350.6/198
- (d) corrrected for pre-study excretion.
- (e) Chlorpyrifos (Uncorrected) = Cumulative 3,5,6-TCP (adjusted for pre-study excretion)/0.36
- (f) Chlorpyrifos (Corrected) = µg Chlorpyrifos (Uncorrected) (5.5 * µg Pre-Study TCPy0.36
- (g) Absorption, µg/kg (Uncorrected) = Chlorpyrifos (Uncorrected)/BW
- (h) Absorption, μg/kg (Corrected) = Chlorpyrifos (Corrected)/BW
- 3.39 μ g/ft², for low and high pressure, respectively). After 8 hours, however, the two pressures yielded similar results. For example, after 8 hours the high pressure sampling dislodged about the same amount as the low pressure (mean = 1.5 μ g/ft² for high pressure,

 $1.35~\mu g/ft^2$ for low pressure). The data for each pressure were pooled to yield an overall mean. The data are presented in Table 4, and the mean values are presented graphically in Figure 1. As shown on this figure, the dislodgeable residues declined approximately one order of magnitude by 96 hours (4 days) post application for both pressures. Dislodgeable residues following granular chlorpyrifos application are much lower than residues resulting from liquid application (e.g., after 48 hours 0.98 - $0.99~\mu g/ft^2$ for granular versus 10.3 and $20.3~\mu g/ft^2$ for low and high pressure liquid, respectively).

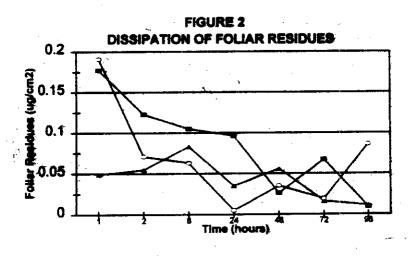
		_		Table 4 ues of Ch & Granule	lorpyrifos				
<u> </u>	Replicate	1 Hrs	2 Hrs	4 Hrs	8 Hrs	24 Hrs	48 Hrs	72 Hrs	96 Hrs
Low Pressure:	Low-1	1.93	1.03	0.75	1.58	0.81	0.56	0.27	0.62
j ,	Low-2	2	1.06	1.37	0.75	0.79	0.43	0.56	0.27
	Low-3	9.75	5.27	0.79	1.72	0.64	1.96	0.78	0.43
·	Mean Low Pressure	4.56	2.45	0.97	1.35	0.7	1.0	0.5	0.44
	Std. Dev.	4.5	2.4	0.3	0.5	0.1	0.8	0.3	0.2
High			-		•				•
Pressure:	High-1	1.91	1.25	1.96	0.82	0.82	0.36	0.3	0.36
	High-2	4.14	1.87	2.07	1.31	1.17	1.68	0.55	_ 0.33
	High-3	10.7	5.62	6.13	2.36	0.98	0.65	0.85	0.58
	Mean High Pressure	5.6	2.9	3.4	1.49	1.0	0.9	0.6	0.42
	Std. Dev.	4.6	2.4	2.4	0.8	0.2	0.7	0.3	0.1

Figure 1



grass samples each at 1, 2, 8, 24, 48, 72 and 96 hours post application. The registrant correlated the weight of each sample to the surface area using a preconstructed regression curve. As noted previously, the grass samples were rinsed with a dilute soap mixture and deionized water, and the liquid was then extracted with ethyl acetate. The foliar residue results are presented on Table 5, and Figure 2. The highest residues were detected 1 hour post application (mean $0.14 \,\mu\text{g/cm}^2$), and dropped slightly to a mean of $0.084 \,\mu\text{g/cm}^2$ by 8 hours post application. Residues from 24 to 96 hours post application were approximately 67-75% lower than the one hour residues and ranged from mean of 0.045- $0.035 \,\mu\text{g/cm}^2$. Individual samples were quite variable, as shown on Figure 2.

Table 5 Summary of Foliar Residues (µg/cm²)							
Hours After Application	1	2	8	24	48	72	96
Replicate 1	0.049	0.055	0.083	0.035	0.056	0.016	0.011
Replicate 2	0.177	0.123	0.105	0.096	0.026	0.067	0.009
Replicate 3	0.191	0.071	0.063	0.005	0.035	0.019	0.086
Mean	0.139	0.083	0.084	0.045	0.039	0.034	0.035



4.2.4 Air Monitoring and Inhalation Exposures

The results of air sampling are presented in Table 6. Samples were collected 9 times during the 96-hour study period. At each time interval both a low (15 in) and a high (60 in) height sample were collected. Samples collected at the lower level tended to be higher than the 60-inch height at all sampling intervals, with exception of the fourth hour concentration collected during football. For this analysis, a 4-hr time weighted average (TWA) was used to estimate inhalation exposures. This average was calculated using an average of the 1-hour samples presented below on Table 6. The registrant calculated exposures using a 2.7 hour TWA concentration sample that was collected during the activities. EPA did not use this sample because the sample is of insufficient duration to characterize exposures, especially during the football session. In addition, the 60 inch 2.7 hr TWA of $0.045~\mu g/m^3$ used by the registrant does not capture the higher concentrations that were apparently present in air during the fourth hour when football occurred of $12.4~\mu g/m^3$. Therefore, 4-hour TWAs of 0.77 and $3.5~\mu g/m^3$ were used to estimate the respiratory component of exposure as shown on Table 7.

Air Concentrations	Table 6 Air Concentrations of Chlorpyrifos Following Application of a 0.5 Percent Granular Insecticide (µg/m³) (a)						
Time (Hours)	Low Height (15 inches)	High Height (60 inches					
0	0.97	0.33					
1	1.06	ND (<0.35)					
2	0.38	1.13					
4	0.66	12.4					
8	0.53	ND (<0.3)					
24	0.52	0.34					
48	。 0.34	ND (<0.29)					
72	0.33	ND (<0.29)					
96	0.52	ND (<0.29)					

ND = not detected (detection limit in parentheses)

(a) Each sample was approximately 60 min

	Table 7 Summary of Inhalation Ventilation Rates and Exposures							
Activity Level	Gender	· · · · · · · · · · · · · · · · · · ·		USEPA Value (a)				
Level		Registrant (L/min)	m³/hr	L/min	Exposure μg (d)			
Rest (b)	Males	7.5	0.4	6.7	0.15			
	Females	6	0.4	6.7	0.15			
Sedentary (c)	Males	not used	0.5	8.3	0.38			
	Females	not used	0.5	8.3	0.38			
Light	Males	20	1.0	16.7	0.39			
į	Females	19	1.0	16.7	0.39			
Heavy	Males	43	3.2	53	22.3			
	Females	-25	3.2	53	22.3			
Total	Males				23.2			
	Females				23.2			

- (a) Values obtained from Exposure Factors Handbook 1997, Volume I, pg. 5-24.
- (b) Resting is defined as lying down. This respiratory rate was used to evaluate 30 min of sunbathing.
- (c) Sedentary defined as sitting and standing. This respiratory rate was used to evaluate 1 hour of picnicking.
- (d) Rest, sedentary and light activity exposures were calculated using the low height 4-hr TWA average of 0.77 $\mu g/m^3$ Exposures from heavy activity, such as frisbee and football (2 hours), were calculated using the high height 4-hr TWA average of 3.5 $\mu g/m^3$.

4.2.4 Hand Rinse

Hand rinse samples were collected at the end of the activity period using the surfactant, dioctyl sodium sulfosuccinate (DSS). These samples were used to estimate the potential oral exposure that might occur from hand to mouth activity of a child. The data are presented in Table 8. The calculations to determine total exposure are presented in Section 4.3. Male volunteers had much higher residues of chlorpyrifos on their hands than female volunteers. For males, the average residues ranged from 2.76 to 9.78 μ g, with an average of 5.62 μ g. In comparison, no residues were detected on any of the four female volunteers (quantitation limit of 0.6 μ g/sample). The overall average of all nine individuals was 3.25 μ g, which is significantly lower than residues detected following the application of liquid chlorpyrifos to lawns of 47.1 μ g.

Table 8 Results of Hand Rinse Sampling of Volunteers After Performance of Activities on Turf Treated with Granular Chlorpyrifos

μ g Chlorpyrifos Found							
Volunteer	Sex	Body Weight (Kg)	Replicate 1	Replicate 2	Average		
G	М	79.45	9.68	9.88	9:78		
Н	М	73.55	5.6	5.58	5.59		
ì	М	79.45	2.74	2.78	2.76		
J	М	81.72	4	3.83	3.92		
К	М	74.91	5.98	6.09	6.04		
L	F	63,56	ND (<0.6)	ND (<0.6)	ND (<0.6)		
М	F	72.64	ND (<0.6)	ND (<0.6)	ND (<0.6)		
N	F	56.75	ND (<0.6)	ND (<0.6)	ND (<0.6)		
0	F	57.20	ND (<0.6)	ND (<0.6)	ND (<0.6)		
Mean (Females)					ND (<0.6)		
Mean (Males)					5.6		
Mean (All)					3.25		
Overall Std. Dev.					3.4		

ND = not detected (quantitation limit presented in parentheses).

4.3 Estimation of Total Exposure, and the Contribution from Different Routes Based on Indirect and Biological Monitoring

4.3.1 Total Exposure and Contribution from Different Routes

The registrant estimated the contribution of the inhalation, dermal, and hand/oral routes to the total exposure using biomonitoring (urine) data, and physicochemical data (air monitoring and hand rinse data). Biological monitoring does not differentiate between the different routes but rather is an indicator of the total internal dose. The contribution of the dermal route was estimated by subtracting the respiratory exposure in Table 7 from the biomonitoring total exposure values obtained from urinary data in Table 3. In order to estimate hand/oral exposure it was assumed that all of the material measured by hand rinse was available for subsequent ingestion. Table 9 combines the results of direct and indirect monitoring and provides an estimate of the contribution

of the various exposure routes. As shown on Table 9, the estimated mean exposures for males and females are 1.2 and 1.7 μ g/kg, respectively. The overall mean exposure is 1.4 μ g/kg, which is much lower than the overall mean exposure resulting from similar exposures to lawns treated with liquid chlorpyrifos of 6.1 μ g/kg (Jaquith 1996).

Estimate		Exposure of Subjected with 0.5%			_	
Volunteer	BW (kg)	Chlorpyrifos Absorbed based on Biomonitoring	Inhalation (a)	Dermal (b)	Oral/Hand (c)	Total Chlorpyrifos Exposure (d)
			Males			
G	79.45	0.69	0.29	0.4	0.12	0.81
<u>———</u> Н	73.55	2.2	0.32	1.9	80.0	2.3
I I	79.45	0.53	0.29	0.24	0.03	0.56
J	81.72	(-1.1) (e)	0.28		0.05	0.33 (g)
K	74.91	0.95	0.31	0.64	0.08	1.0
Mean	77.81		0.3			1.2
			Females	`		
L	63.56	0.87	0.37	0.5	0.005 (f)	0.86
M	72.64	0.67	0.32	0.35	0.005 (f)	0.67
N	56.75	1.53	0.41	1.1	0.005 (f)	1.5
О	57.2	3.7	0.41	3.3	0.005 (f)	3.7
Mean	62.54		0.38		·	1.7

- (a) Inhalation exposure is based on 23.2 μ g for males and females, which was divided by body weight.
- Dermal exposure (μ g/kg) =Total chlorpyrifos absorbed (μ g/kg) from biomonitoring data minus estimated inhalation exposure (μ g/kg).
- (c) Based on hand rinse data divided by body weight.
- (d) Sum of chlorpyrifos dose absorbed based on biomonitoring data and oral/hand data.
- (e) Estimated background exposure exceeds chlorpyrifos exposure from study activities.
- (a) Assumes exposure at ½ the detection limit.
- (b) Value excludes dermal exposure, and is not included in the overall mean.

4.3.2 Extrapolation of Exposure from Adults to Children

The registrant extrapolated from the estimated respiratory, dermal and handwash data for adults to derive an estimate of the potential exposure of a one year old child. This analysis evaluates a child ages 1-6 years old consistent with EPA guidance. The assumptions used for this extrapolation are shown on Table 10. The calculations for estimating a child's exposure are similar to those used to estimate the adults exposure and the results are presented in Table 11. For this extrapolation, the estimated respiratory exposure contribution was subtracted from the total exposure, yielding an estimate of dermal exposure. The estimates of exposure via the dermal route were then adjusted to account for surface area differences between adults and children. Oral exposure via hand to mouth activity was estimated by assuming that all of the pesticide removed by hand rinse was available for ingestion. For child exposures, the adult oral exposure estimates were also adjusted to account for the hand surface area differences between adults and children. EPA also used this approach to estimate child exposures. As shown on Table 11, the mean extrapolated exposure to a 1-6 year old child is $2 \mu g/kg$, with a range of 0.75 to 5.1 $\mu g/kg$, which is slightly greater than the exposures estimated for adults.

	Exposu	re Assumpt	Table 10 ions used to Estimate Child	Exposures
Parameter	Males	Females	Percentage of Adult Value	Basis of Child Parameter
Total Skin Surface Area	7,730 cm ²	7,630 cm ²	35% for males; 38% for females (Assumes 90 th percentile total surface area of 22,000 and 19,800 cm ² for adult males and females, respectively from EFH, p.6-13)	50th percentile of ages 2-6. Exposure factors Handbook (EFH), 1997, p. 6-15. Adult values recommended in Draft OPP Standard Operating Procedures for Residential Exposure Assessments, 1997, p. 55.
Hand Surface Area	356	O cm²	43% for females and 39% for males (Assumes 50th percentile hand surface area of 817 and 909 cm ² for adult females and males, respectively, from EFH, p. 6-13).	50th percentile for a toddler age 3. Value recommended Draft OPP Standard Operating Procedures for Residential Exposure Assessments, 1997, p. 21. Represents average of ages 2-4 from EFH 1997.
Body Weight	1:	5 kg	Individual Specific	Mean of the median values for male and female 1-6 year old children. Value recommended in Draft OPP Standard Operating Procedures for Residential Exposure Assessments, 1997, p. 22.
Inhalation Rate: Rest (30 mm)	0.3	m³/hr	75%	Recommended averagely hour inhalation rates for children 0-18 yrs. Exposure Factors Handbook,
Sedentary (60 min)	0.5	m³/hr	100%	Volume 1 p. 5-24.
Light Activity (30 min)	11	n³/hr	100%	
Heavy Activity (120 min)		m³/hr	60%	
TWA Inhalation Rate	1.24	m³/hr		

			Chlorpyrifos based vironmental Data	on
		Extrapolat	ed Value to Child	
Volunteer	Inhalation (a)	Dermal (b)	Oral/Hand (c)	Total Chlorpyrifos Exposure (d)
		Males		
G	0.25	0.74	0.25	1.24
Н	0.25	3.3	0.15	3.7
Ī	0.25	0.44	0.06	0.75
J	0.25	— (e)	0.11	0.36 (g)
Κ.	0.25	1.1	0.16	1.5
Mean	0.25			1.8
		Females		
L	0.25	0.79	0.009 (f)	1.05
М	0.25	0.64	0.01 (f)	0.9
N	0.25	1.6	0.008 (f)	1.8
0	0.25	4.8	0.008 (f)	5.1

(a) Inhalation exposure is based on the low height of 0.77 μ g/m³, a TWA inhalation rate of 1.24 m³/hr., 4 hours exposure and 15 kg body weight.

2.2

(b) Dermal exposure (μ g/kg) = Adult dermal dose (μ g/kg) X Adult BW/15 kg child BW X ratio of child to adult surface area (0.35 males and 0.38 females).

(c) Child oral exposure = estimated adult oral dose X adult BW/15 kg child BW X ratio of child to adult hand surface area (0.43 for females and 0.39 for males). Exposure neglects incidental ingestion of granules and/or soil containing chlorpyrifos.

(d) Sum of inhalation, dermal and oral exposure.

0.25

Mean

Overall Mean

(e) Estimated background exposure exceeds chlorpyrifos exposure from study activities.

(a) Assumes exposure at ½ the detection limit.

(b) Value excludes dermal exposure, and is not included in the overall mean.

5.0 FIFRA 1988 CHECKLIST COMPLIANCE

Compliance with Sections 132 and 133 of Subdivision K (Exposure: Re-entry Protection) of the Pesticide Assessment Guidelines (U.S. EPA, 2984) is critical if a study is to be considered acceptable to the Agency. The itemized list below describes compliance with the major points of Subdivision K. The list is based on the checklist for "Residue Dissipation Data" used for study reviews by the U.S. EPA/OPP. In addition, this study is considered to be a biomonitoring study, which does not specifically have a FIFRA checklist.

Typical end-use product of the active ingredient tested. This criterion was met as a granular formulation of 0.5% chlorpyrifos at a rate of approximately 1.8 lb active ingredient per acre was used in the study.

End-use product applied by application method recommended for the turf. Application rate given and should be at the least dilution and highest, label permitted, application rate. This criterion was met as the single application was made to turf. The intended application rate used was ~1.8 lb ai/acre, although the deposition measurements indicate that only 75% of the theoretical recommended label rate was applied to the field where exposure activities occurred. The application rate, however, is within the typical variability of the equipment used for application.

Site(s) tested representative of reasonable worst-case climatic conditions expected in intended use areas. The study took place in Midland, Michigan, presumably during the summer months as the participants wore shorts and short sleeved shirts. It is questionable whether the weather during the testing period was representative of "worst case," although the conditions were considered appropriate for typical residential exposures.

Application(s) occurred at time of season that the end-use product is normally applied to achieve intended pest control. This criterion was met.

Meteorological conditions including temperature, wind speed, daily rainfall, and humidity provided for the duration of the study. This criterion was met.

Duplicate foliar and/or soil samples collected at each collection period. This criterion was met as triplicate samples were collected for each time period.

Sufficient collection times to establish dissipation curve. First sample time taken as soon as dusts settle. Short durations should exist between earlier sample intervals and may lengthen with later samples. This criterion was met as samples were taken at 1, 2, 8, 24, 48, 72 and 96 hours post-application.

Control and baseline foliar samples collected. Blank samples, in addition to samples

spiked with known quantities of chlorpyrifos were analyzed as part of quality assurance.

Residue storage stability, method efficiency (residue recovery), and limit of quantification provided. This criterion was partially met as method efficiency and limit of quantitation were provided. Residue storage stability data were not provided, although, all the samples were stored on ice prior to analysis.

- Soil residue data expressed as $\mu g/g$ of fine soil material. This criterion is not applicable to the study.
- Foliar residue data expressed as μg or mg/cm^2 leaf surface area. This criterion was met as all FDR data were as $\mu g/cm^2$.
 - Reported residue dissipation data in conjunction with toxicity data must be sufficient to support the determination of a reentry interval. This criterion was met.

6.0 REFERENCES

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ce: Correspondence file Chlorpyrifos file

APPENDIX A

RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF

TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI per ACRE

VOLUNTEER G [BW (kg) = 79.45]

Sample		Urine Weight			Cred	atinine	3,5,6-TCP	
	Final (g)	Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	1660	82.8	1577	12	76	30.2	5.2	8.2
2	770	81.8	688	12	<i>151</i>	26.2	8	5.51
3	533	83.4	450	9	206	<i>31.1</i>	<i>15.2</i> .	6.83
4	502	83.7	418	11.5	238	26.1	23.4	9.79
5	569	84.8	484	12	224	27.3	22.7	10.99
6	572	82.4	490 ~	12	195	24	18.9	9.25
7	539	81.3	458	12	221	25.5	18.5	8.47
. 8	1089	<i>82.3</i>	1007	12	117	29.7 .	8.5	8.56
9	869	84.2	<i>785</i>	12	129	25.5	9.6	7.53
10	499	81.9	417	11.5	187	20.5	14.2	5. <i>92</i>
11	851	83.3	<i>768</i>	12.33	190	<i>35.7</i>	10.9	8.37
12	431	80.6	350	12	227	20	16.4	5.75
<i>13</i>	554	81.5	473	12	260	- 31	17.5	8.27
14	323	82.7	240	12	388	23,5	22.1	5.3
			Total Days	6.8	AVG =	26.9	SUM =	108.74

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RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF

TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI

per ACRE

 $VOLUNTEER\ H\ [BW\ (kg)=73.55]$

Sample		Urine Weig	ght	Duration	Стеа	utinine	3,5,6-TCP	
	_Final	(g)Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	NA	84.8	1040	14.67	81	18.7	6.7	6.97
2	NA	83.2	1007	12.83	<i>87</i>	22.3	7.1	7.15
3	NA	85.6	455	12	178	22	24.7	11.25
4	NA	82.6	485	12.5	171	21.6	28.8	13.98
5	NA.	82.8	615	13.5	146	21.7	22.1	13.6
6	NA.	84.1	1777	12	<i>55</i>	26.6	6.9	12.26
7	NA	85.9	910	11.67	91	23.2	13.6	12.38
8	NA	84.4 %	1037	10.83	72	22.5	10	10.37
9	NA	81.2	671	13.17	139	23.1	22.2	14.89
10	NA	81.8	1313	12.42	64	22.1	8.6	11.29
11	NA	<i>85.1</i>	560	9.42	123	23.9	. 14.1	7.89
12	NA	81.8	1149	12.5	121	36.3	9.6	11.03
13	NA	84.5	772	14.33	142	25	13.5	10.42
14	NA	83.1	564	9.66	103	19.6	11.4	6.43
			Total Days	7.1	AVG =	23.5	SUM =	149.91

NA = not available

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RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF
TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI

per ACRE

VOLUNTEER I [BW (kg) = 79.45]

Sample	•	Urine Weig	ght	Duration	Creatinine		3,5,6-TCP	
	Final (g	Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	1833	84.5	1749	12.34	55	23.5	4.8	8.39
2	1028	84.2	944	11.66	92	22.5	8.8	8.31
3	644	80.2	564	9	141	26.7	14.8	8.34
4	814	83.4	<i>731</i>	10.25	116	25	10.7	7.82
5	1384	84.8	1299	12.5	77	24.2	7.4	9.61
6	1389	82.3	1307	11.5	69	<i>23.7</i>	7.3	9.54
7	1099	86.1	1013	13.75	108	24	10.6	10.74
8	433	82.4	351	11	248	23.9	32	11.22
9	1253	84.2 =	1169	13	92	25	10.2	11.92
10	1094	83.3	1011	12	102	26	8.9	9
11	673	84.7	588	11	149	24.1	11.3	6.65
12	1698	84.7	1613	13	66	24.7	4.7	7.58
13	1554 ·	82.1	1472	10.5	62	26.3	4.9	7.21
14	971	82.4	889	12	109	24.4	8.2	7.29
	,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,,		Total Days	6.8	AVG =	24.6	SUM =	123.62

APPENDIX A

RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF

TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI

per ACRE

VOLUNTEER J[BW (kg) = 81.72]

Sample	. 1	Urine Weig	ght	Duration	Crea	Creatinine		-TCP
	Final (g	Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	826	82.4	744	10	144	31.5	36.5	27.16
2	882	82.7	799	14.42	161	26.2	27.3	21.81
3	487	84.3	403	6.5	166	30.2	27.7	11.15
4	963	85.2	878	14.5	162	28.8	29.3	25.72
5	712	84.3	628	12	178	27.3	31.1	19.52
6	858	84.9	773	10.25	142	31.5	20.1	15.54
7	<i>739</i>	82.7	656	14.25	167	22.6	41.6	27,3
8	· 335	84.6	250	11.67	197	12.4	35.3	8.84
9	674	84.5	590	10.25	173	29.2	38.6	22.75
10	1074	82. <u>I</u>	992	13.58	143	<i>30.7</i>	26.7	26.48
11	827	82.2	745	10	140	<i>30.6</i>	25.1	18.69
12	864	83.1	781	13	<i>151</i>	26.6	28.9	22.57
13	844	82.3	762	12.17	168	30.9	27.6	21.02
14	826	85	741	12.67	175	<i>30.1</i>	23.1	<i>17.</i> 12
			Total Days	6.9	AVG =	27.8	SUM =	285.67

APPENDIX A

RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF

TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI per ACRE

VOLUNTEER K [BW (kg) = 74.91]

Sample		Urine Weight			Cre	atinine	3,5,6-TCP	
	Final (g	Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	611	84.4	527	12	259	36.4	7.1	3.74
2	477	84.9	392	12	183	19.2	10,2	4
3	447	80.6	366	12	228	22.3	14	<i>5.13</i>
4	185	85.9	99	12	198	5.2	15.9	1.58
5	896	85.2	<i>811</i>	12	156	33.8	14	11.35
6 -	380	82.8	297	12	306	24.3	29	8.62
7	503	81.1	422	12	238	26.8	17.2	7.26
8	608	82.5	526	. 12	161	22.6	12.I	6.36
9	561	<i>85.4</i>	476	12	202	25.7	13	6.18
10	392	81.6	310	12	178	14.7	10.8	3.35
11	436	83.2	35 3	12	286	27	13	4.59
12	402	84.7	317	12	260	22	11.5	3.65
13	<i>753</i>	82.8	670	12	195	<i>34.9</i>	10.5	7. 04
14	305	83.1	222		275	16.3	12.5	2.77
		`	Total Days	7.0	AVG =	23.7	SUM =	75.62

APPENDIX A

RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF

TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI

per ACRE

VOLUNTEER L[BW (kg) = 63.56]

Sample	Urine Weight			Duration	Crea	tinine	3, 5, 6	-TCP
	Final (g)Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	893	84.1	809	9.25	70	23.1	6.1	4.93
. 2	921	81.3	840	12	74	19.6	5.7	4.79
3	259	82	177	12	180	10	<i>17.1</i>	3.03
4	1162	84.3	1078	12	59	20	6.1	6.57
5	872	82.4	790	12	69	17.1	7.3	5.76
6	865	83	782	12	-88	21.7	9	7.04
. 7	78 i	82.3	699	12	78	17.2	<i>7</i> .8	5.45
. 8	943	82.4 ₀	861	12	6.8	18:4	9.2	7.92
9	638	83.4	555	12	103	18	13.8	7.65
10	524	84.6	439	. 12	137	18.9	14.7	6.46
11	585	83. Î	502	12	111	17.5	11.9	5.97
12	717.	83	634	12	83	16.6	8.6	5.45
13	1064	82.9	981	12	78	24.1	7.2	7.06
14	1053	83.4	970	. 12	58	17.7	4.8	4.65
· · · · · · · · · · · · · · · · · · ·			Total Days	6.9	AVG =	18.6	SUM =	82.73

APPENDIX A

RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF
TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI

per ACRE

VOLUNTEER M [BW (kg) = 72.64]

Sample		Urine Weig	ght	Duration	Crea	utinine	3,5,6-TCP	
:	Final (g	Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	849	82.6	766	9.25	97	26.55	4	3.07
2	681	84.4	· 597	12	125	20.53	5.2	3.1
3	559	81.6	477	6	112	29.44	7.1	3.4
4	660	84.3	<i>576</i>	12	128	20.3	7.8	4.5
5	583	84	499	12	154	21.16	10.7	5.3
6	446	84.3	362	12	226	22.51	16.3	5.9
7	1440	84.6	1355	12	58	21.64	4.6	6.2
8	871	82.3°	789	12	62	13.46	4.1	3.2
9	805	83	722	12	138	27.43	7.8	5.6
10	1399	85.1	1314	12	62	22.43	3.2	4.2
11	<i>738</i>	82.4	656	12	130	23.47	5.6	3.7
12	559	84.7	474	12	101	13.19	3.9	1.8
13	1075	82.8	<i>9</i> 92	12	124	<i>33.87</i>	5	5
14	437	82.4	355	12	272	26.56	7.7	2.7
			Total Days	6.6	AVG =	23.0	SUM =	57.67

APPENDIX A
RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF
TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI per ACRE

VOLUNTEER N [BW (kg) = 56.75]

Sample		Urine Weight			Cre	atinine	3,5,6	-TCP
	Final (g)	Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
1	765	81.5	684	12	74	17.8	5.5	3.8
2 ·	995	84.5	911	12	47.	15.1	3	2.7
3	461	83.7	<i>377</i>	12	106	14.1	<i>7</i> .5	2.8
4	1038	81.9	956	12	78	26.3	7.8	7.5
5	1056	85.3	971	12	60	20.5	6.5	6.3
6	1671	83.2	1588	· 12	39	21.8	4.3	6.8
7	721	82.9	638	12	122	27.4	10.5	6.7
8	2543	82.8	2460	12	23	19.9	2.7	6.6
9 `	1446	82.2	1364	12	56	26.9	<i>5.3</i>	7.2
10	1681	84.1	1597.	12	24	13.5	2.2	3.5
11	1215	83.3	1132	12	86	34.3	6.1	6.9
12	2576	82.5	2494	12	21	18.5	1.4	3.5
13	675	82.5	593	12	149	31.1	7	4.2
14	1331	82.2	1249	12	60	26.4	4.1	5.1
			Total Days	7.0	AVG =	22.4	SUM =	73.6

APPENDIX A
RESULTS OF URINE MONITORING OF VOLUNTEERS PERFORMING ACTIVITIES ON TURF
TREATED WITH A GRANULAR FORMULATION OF CHLORPYRIFOS AT A RATE OF 2 LBS AI

per ACRE

VOLUNTEER O [BW (kg) = 57.2]

Sample		Urine Weig	ght	Duration Crea	tinine	3,5,6	-TCP	
	Final	(g)Tare (g)	Net (g)	(hrs)	(mg/dL)	mg/kg/day	(ng/g)	ug
I	1086	83.6	1002	12	63	22.08	7.3	7.3
2	937	82.7	854	12	58	17.32	6.5	5.6
3	840	83.5	<i>757</i>	6	47	24.86	5.8	4.4
4	1185	80.8	1104	12	54	20.85	6.5	7.2
5	1059	84.2	975	12	58	19.77	<i>7.3</i>	7.1
6	1179	84.2	1095	12	60	22.97	7.4	8. I
7	1005	82.5	923	<i>12</i> .	60	19.35	7.2	6.6
8	<i>831</i>	81.9 _~	749	12	79	20,69	9.7	7.3
9	522	83.3	439	12	79	22.7	77	33.8
10	639	82.3	557	12	94	18.3	30.4	16.9
11	1325	82.8	1242	12	54	23.45	<i>15.3</i>	19
12	803	82	<i>721</i>	12	83	20.92	20.4	14.7
13	1462	84.4	1378	12	48	23.12	9.4	13
14	809	83. <i>7</i>	<i>725</i>	12	65	16.48	10.7	<i>7.8</i>
			Total Days	6.8	AVG =	20.9	SUM =	158.8

APPENDIX B

Pharmacokinetic Model Used by DowElanco to Estimate the Amount of Chlorpyrifos Absorbed After Exposure

Xu(t) = Ka * fXo [1/Ka + Exp (-Kt)/(K-Ka) - K *exp (-Ka*t) / (Ka*(K-Ka))]Where:

t = time in hours

K = 0.0258 = rate constant for elimination, per hr

Ka = 0.0308 = rate constant for absorption, per hr

f = 0.72 = fraction of absorbed dose excreted as 3,5,6-TCP

Xo = 1

Days	Hours	Ka*f	1/ K a	exp(-Kt)/	-K*exp(-Ka*t)/	Cum. Exc.	Int Excr.
	Pos	t		(K-Ka)	Ka*(K-Ka)	Xut(t)	Xut(t)-
	Dosing	<u> </u>	<u></u>	:			Xut(t-1)
	0	0.0222	32.47	-200.00	167.53	0.000 0	0.0000
	12	0.0222	32.47	-146.75	115.77	0.0331	0.0331
1	24	0.0222	32.47	<i>-107.67</i>	80.00	0.1064 -	0.0733
	36	0.0222	32.47	·· -79.01	<i>55.28</i>	0.1941	0.0877
2	48	0.0222	32.47	-57.97	38. 20	0.2820	0.0879
	60	0.0222	32.47	-42.53	26.40	0.362 6	0.08 06
3	<i>72</i>	0.0222	32.47	-31.21	<i>18.24</i>	0.4329	0.07 03
	84 '	0.0222	32.47	-22.90	<i>12.60</i>	0.4922	0.0593
4	96	0.0222	32.47	-16.80 -	<i>8.71</i>	0.5412	0.0490
	108	0.0222	32.47	-12.33	6.02	0.58 08	0.0396
5	120	0.0222	32.47	-9.05	4.16	0.6124	0.0316
	132	0.0222	32.47	-6.64	2.87	0.6372	0.0248
	133	0.0222	32.47	-6.47	2.79	0.6394	0.0020
6	144	0.0222	32.47	-4.87	1.99	0.6569	0.0197
	156	0.0222	32.47	-3.57	1.37	0.6719	0.01 50
7	168	0.0222	32.47	-2.62	0.95	0.6837	0.0118
	180	0.0222	32.47	-1.92	0.66	0.6928	0.0091
8	192	0.0222	32.47	-1.41	0.45	0.69 95	0.0 <mark>067</mark>
	204	0.0222	32.47	-1.04	. 0.31	0.7047	0.0052
9	216	0.0222	32.47	<i>-0.76</i>	0.22	0.708 8	0.0041
	2 28	0.0222	32.47	-0.56	0.15	0.7118	0.0030
10	240	0.0222	32.47	-0.41	0.10	0.7140	0.0022



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